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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B27K 7/00, B67B 1/03	A1	(11) International Publication Number: WO 00/64647 (43) International Publication Date: 2 November 2000 (02.11.00)
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(54) Title: TREATED CLOSURES I (57) Abstract In a first aspect, the present invention provides a method for producing a coating or diffusion layer on a substrate (e.g. a cork) for use in contact with a food product or beverage, said coating or diffusion layer preventing or inhibiting passage therethrough (e.g. from a cork to an alcoholic beverage) of flavour-active or odour-active compounds (commonly known as cork taint), and said method comprising applying to the surface of said substrate an effective amount of a barrier polymer, said barrier polymer being a polymeric material, the molecular structure and/or morphology of which prevents or inhibits passage therethrough of flavour-active or odour-active compounds. In a second aspect, the present invention provides a coated substrate, and in particular a coated natural or synthetic cork, produced according to that method.		

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TREATED CLOSURES 1

BACKGROUND TO THE INVENTION

This invention provides improved closures for use in connection with food or beverages. One application is in relation to closures for wine bottles.

Wine bottles have traditionally been stoppered with corks made from natural cork material. However, this material can be subject to initial flaws, or deteriorate in use, resulting in contamination or spoilage of the wine. For example, oxidation of the wine, due to permeation of oxygen through the cork into the wine, results in vinegar flavour. "Cork taint", due to the presence of trichloro-anisoles (TCA) and other undesirable flavour-active or odour-active compounds in the cork, imparts a musty or mouldy smell and flavour to the wine. Leakage can also be a problem. Furthermore, cork is a relatively expensive material, as most supplies still come from Portugal.

None of the alternatives to natural corks proposed to date have been entirely satisfactory.

Synthetic "corks" and screw-cap stoppers have been used in the wine industry, but have not yet been tested adequately over the prolonged storage periods of quality red wines. There is some indication, however, that synthetic "corks" may impart flat flavours to wines. Furthermore, there is considerable consumer resistance to use of synthetic "corks" and screw-cap stoppers, particularly for quality wines. A further disadvantage is that synthetic "corks" are generally far more difficult to remove, using a hand-operated corkscrew, than natural corks.

Accordingly, there have been numerous attempts to improve on natural cork stoppers, by coating or impregnating them.

The first cork coatings were simply lubricants such as paraffin and Vaseline. These merely ensured that the cork was easier to insert into the bottle and later remove,

without disintegration. The other problems associated with cork stoppers were not addressed.

Currently, materials used in surface treatment of corks include oils and silicone resins, emulsions of various formulations, as well as some synthetic coatings. These coatings do prevent leakage of the wine, but do not provide a barrier against taint and oxidation.

Many of these coatings also present problems with the coating coming off the cork and leaving an oily layer on the wine surface.

Hybrid corks have been moulded from natural cork and synthetic cork cells made from a synthetic polymer. The synthetic cells fill the gaps between the cork cells, and a binding agent (such as polyurethane) is used to bind the cells together. However, hybrid corks have to date proved unsatisfactory, as they often leak and can disintegrate and be difficult to extract from a bottle.

The present invention provides an improved closure having a surface coating or diffusion layer comprising an appropriate polymer. This coating or diffusion layer has many properties which are of benefit when used (for example) in relation to corks (either natural or synthetic) for wine bottles. The coating or diffusion layer limits oxygen permeability, inhibits or prevents the diffusion of trichloro-anisoles (TCA) and other flavour-active or odour-active compounds from the cork to the alcoholic beverage, adheres strongly to the cork and/or penetrates into the surface of the cork, is sufficiently flexible to be capable of withstanding compression and decompression during the corking process, enables the coated cork to be readily extracted from the bottle, reduces or prevents wine leakage, is resistant to sulphur dioxide, and has long life under alcoholic beverage conditions.

These coatings or diffusion layers are also applicable to substrates other than cork (eg packaging and wrapping materials) which are in contact with food products or beverages.

SUMMARY OF THE INVENTION

According to the present invention, an appropriate polymer, which forms a physical barrier to gases (eg oxygen) and flavour-active or odour-active compounds (eg TCA), is applied as a surface coating or diffusion layer to a substrate for use in contact with food products or beverages. Polymeric materials, the molecular structure and/or morphology of which help to prevent permeation of gases and vapours (such as oxygen) and flavour-active or odour-active compounds (commonly known as taint compounds), can be classed as barrier polymers. Barrier polymers with low oxygen permeability (see R.Tajima, A.Banba, M. Takanori, T. Amachi, M.Masuda and T.Izumi, Nippon Hosokagakkaishi (1994), 3 (1), 45-55) have also been shown to prevent the migration of "taint" through the polymer (eg from a coated cork to an alcoholic beverage). Polymeric films with barrier properties can be applied to cork or other substrates to provide a barrier against ingress of "taint" compounds into the food product or beverage.

In a first aspect, the present invention provides a method for producing a coating or diffusion layer on a substrate (eg a cork) for use in contact with a food product or beverage, said coating or diffusion layer preventing or inhibiting passage therethrough (eg from a cork to an alcoholic beverage) of flavour-active or odour-active compounds, and said method comprising applying to the surface of said substrate an effective amount of a barrier polymer, said barrier polymer being a polymeric material, the molecular structure and/or morphology of which prevents or inhibits passage therethrough (eg from a cork to an alcoholic beverage) of flavour-active or odour-active compounds.

In a second aspect, the present invention provides a coated substrate, and in particular a coated natural or synthetic cork, produced according to that method.

The substrate may, for example, be a bottle closure (such as a cork), packaging and wrapping materials (such as packaging for cheese), or a bottle or other container.

As mentioned above, the polymer is selected so as to form a physical barrier to the passage of gases and flavour-active or odour-active compounds. In particular, the polymer coating or diffusion layer of the present invention will prevent any flavour-active or odour-active compounds migrating from a cork to an alcoholic beverage. It must also adhere strongly to the substrate and/or penetrate into the surface of the substrate, and be sufficiently flexible for its proposed use (eg to withstand compression and decompression during the corking process, if the substrate is a cork). Furthermore, if the substrate is a cork, the polymer coating or diffusion layer must enable the coated cork to be readily extracted from the bottle, prevent wine leakage, and have long life under alcoholic beverage conditions. Preferably, the polymer coating or diffusion layer will also be resistant to sulphur dioxide and changes in pH.

DETAILED DESCRIPTION OF THE INVENTION

Polymers which may be used include:

- polyurethane and copolymers and ionomers
- polyethylene terephthalate (PET)
- polyethylene vinyl alcohol
- polyvinyl alcohol
- polyacrylonitrile and copolymers, eg styrene-acrylonitrile and acrylonitrile-butadiene-styrene (ABS)
- polyvinylidene chloride (PVDC) and copolymers
- polyvinylchloride and copolymers
- Cellophane

Saran (a vinylidene chloride-vinyl chloride copolymer)

epoxy polymers

siloxane copolymers, eg comprising polyethylene glycol (PEG), isoprene,

butadiene, lactone, amino, terephthalate, amino acid, heterocyclic, hydride

(SiH), thiol or epoxy functionalities

monofunctional, difunctional and polyfunctional silanes, eg $(\text{RO})_3\text{SiNH}_2$

wherein R is alkyl, and copolymers

polyamides, eg nylons, and copolymers

polychlorotrifluoroethylene

bisphenol A (BPA)-epichlorohydrin

polyacetal

polyvinylfluoride

polymethylmethacrylate and copolymers

cellulose nitrate and derivatives

poly (isobutylene) and copolymers

polyisoprene

polyvinylacetate (PVA) and copolymers

polybutadiene and copolymers

lamine films comprising polyethylene, polyethylene terephthalate (PET),

polyethylene vinyl alcohol and/or polyamide copolymers.

functionalised and unfunctionalised polysilsesquioxanes, examples of which are disclosed in the following references:

Feher, F.J. and Budzichowski, T.A., J. Organometal. Chem., 379:33-40, 1989

Feher, F.J., Wyndham, K.D., Soulivong, D. and Nguyen, F., J. Chem. Soc. Dalton Trans., 1491-1497, 1999

Feher, F.J., Schab, J.J., Soulivong, D. and Ziller, J.W., Main Group Chemistry, 2:123-132, 1977.

Polyethylene vinyl alcohol has been found to be particularly suitable.

Modifications of the polymers may be necessary to improve resistance to reactions with various components of the food product or beverage (eg wine).

The polymer coatings and diffusion layers of the present invention may be used in conjunction with lubricants, such as paraffin or Vaseline, to make the coated cork easier to insert into a bottle and later extract.

The method of applying the polymer to the substrate will be dependent on the nature of the polymer and of the substrate, and will include such conventional processes as film formation, adsorption from solution, reactive-adhesion to cork, melt polymer application (eg thermoforming, vacuum forming and plasma polymerisation), UV curing and Corona discharge processes. The polymers may also be components of multilayer laminate structures.

Preferably, the substrate (eg cork) is prewashed with a solution (eg ethanol, water or a mixture of ethanol and water) and then dried before coating, to remove any surface contamination.

The following examples form an overview of some of the technologies which may be used. These examples are illustrative, but not restrictive, of the present invention.

DESCRIPTION OF THE DRAWINGS

FIG 1 is the result of Scanning Electrode Microscopy (SEM) of the coating of Example 1.

FIG 2 is the result of SEM of the coating of Example 2.

FIGS 3A-D are the results of SEM of the coating of Example 3.

SENSORY EVALUATION TESTS

Corks were spiked with TCA by soaking 100 corks in 1.5 litres of a 100mg/L solution of TCA in absolute ethanol for 24 hours. The corks were then removed from the solution

and allowed to dry in a 40°C oven for 24 hours before being submitted for sensory evaluation to ensure that the corks have TCA odours. These corks were then coated with the coatings described below and sent for sensory evaluation.

Coated TCA spiked corks were immersed in approximately 150mL of white wine for 24 hours. The wine was evaluated for unacceptable odours by a team of experts, being a group of no less than three qualified trained sensory evaluators. The samples were given a rating of between 1 and 4. A rating 1 indicated a slight odour, rating 2 a moderate odour, rating 3 a strong odour and rating 4 a very strong odour. A rating of 2 or less was acceptable. The sensory evaluation tests related primarily to TCA odours, which were indicative of likely problems relating to undesirable flavour- and odour-active compounds.

COATINGS

A TCA spiked cork and a non-TCA cork were coated with the coatings described below and subjected to sensory evaluation.

Example 1: Bistrimethoxysilypropylamine



A solution of 10% Bistrimethoxysilypropylamine in ethanol was stirred while water (adjusted to pH 10 using sodium hydroxide) was added. The corks were immediately dipped into the solution and allowed to cure in an oven at 80°C for 30 minutes.

Sensory evaluation tests gave a rating of 2 or less.

Scanning Electrode Microscopy (SEM) results showed a continuous layer of coating on the cork surface (Fig 1.)

Example 2: Two Dip Process (Bistriethoxysilane/Aminopropyltriethoxysilane)

This was a two dip process. A bistriethoxysilane (BTSE) solution was prepared by adding ethanol to a 5% BTSE-in-water solution adjusted to a pH of 10 with acetic acid. The solution was allowed to hydrolyse for 48 hours. A TCA spiked cork was dipped into this solution and quickly dried with compressed air. Next, the cork was dipped into a 2% aminopropyltriethoxysilane-in-water solution, which had been allowed to hydrolyse for 48 hours. The cork was then cured in an 80°C oven for 10 minutes.

Sensory evaluation tests gave a rating of 2 or less.

A sample coated cork was analysed by SEM. The results are shown in Fig 2.

Example 3: Polyvinylacetate/Polymethylhydrogen Siloxane Emulsion

The coating formulation consisted of a mixture of 75mL of polyvinylacetate emulsion (PVA) and 25mL of polymethylhydrogen siloxane emulsion. 100 corks were placed into a tumbler and 20mL of the coating formulation was distributed casually over the corks. The corks were tumbled, to evenly distribute and dry the coating, for 1 hour at 40°C.

Sensory evaluation and Gas Chromatography/Mass Spectroscopy (GC/MS) results showed that no TCA or other undesirable odours were present. In particular, sensory evaluation tests gave a rating of 2 or less.

The SEM showed a visible uniform coating on the surface of the cork (Fig 3A). The coating was also visible in cracks on the surface of the cork (Fig 3B). Analysis of the coating after it had been immersed in white wine for 24 hours showed that the coating was still present and intact (Fig 3C). After compression in a commercial hand corking device, the coating still formed a continuous layer (Fig 3D).

Example 4: Polyurethane

A mixture of 1,3-Bis(aminopropyl)tetramethyldisiloxane (3g, 0.012mol) and caprolactone (4.1g, 0.036mol) was heated to 75°C under nitrogen before the catalyst, stannous octoate (0.1mL), was added. The mixture was refluxed for 2 hours at 75°C before the temperature was raised to 140°C for a further 1.5 hours. The product was then allowed to cool.

A mixture of the above product (7g, 0.012mol), dimethylolpropionic acid (0.8g, 5.95×10^{-3} mol), hexamethylenediisocyanate (3g, 0.018mol), acetone (20mL) and dibutyltin dilaurate (0.1mL) was stirred under nitrogen at 35°C for 15 minutes and then allowed to cool. Triethylamine (1mL) was added and stirred continuously for 30 minutes, before slowly adding 30mL of distilled water. The acetone was removed *in vacuo* to give the water-dispersed polyurethane.

Corks were dipped into this coating and allowed to cure in an oven at 40°C for 24 hours.

Sensory evaluation tests gave a rating of 2 or less.

Example 5: Polybutadiene/Triethoxysilane Copolymer

A mixture of polybutadiene ($M_n = 400$, 9.1g, 0.023mol), triethoxysilane (4.2g, 25mmol) and H_2PtCl_6 (0.8mL), in toluene, was refluxed for 24 hours under nitrogen at 110°C. The solution was then allowed to cool, and solvent and excess triethoxysilane was evaporated under vacuum to give a pale yellow oil as a product.

The polymer was diluted to 25% (v/v) with ethanol and the cork was dipped into this coating and then dried at 40°C for 24 hours.

Sensory evaluation tests gave a rating of 2 or less.

Example 6: Preparation of EVOH-OC(O)NH(CH₂)₃Si(OEt)₃

Polyethylene vinyl alcohol (EVOH) film (9g) was placed into a reaction vessel and purged with nitrogen for several minutes. Toluene (280mL), isocyanatopropyltriethoxysilane (10mL) and dibutyltin dilaurate (1mL) were added and the reaction was allowed to proceed under nitrogen at 50°C for 24 hours. The film samples was then washed with tetrahydrofuran (THF) (3x15mL), tert-butyl alcohol (2x15mL), toluene (2x15mL) and dried under vacuum (10 hours). The film was wrapped around the cork, and then sealed with a heat gun.

Sensory evaluation tests gave a rating of 2 or less.

Example 7: Partial co-hydrolysis and condensation of TMOS and EVOH-OC(O)NH(CH₂)₃Si(OEt)₃

A solution of tetramethoxysilane (TMOS) (10mL) in tert-butyl alcohol (86.6mL), water (12.2mL) and hydrochloric acid (0.2mL) was added to EVOH-OC(O)NH(CH₂)₃Si(OEt)₃ film in a reaction flask. The reaction was allowed to proceed for 48 hours at room temperature, washed with tert-butyl alcohol (3x5mL), water (3x5mL) and toluene (3x15mL), and dried under vacuum for 6 hours. The film was wrapped around the cork, and then sealed with a heat gun.

Sensory evaluation tests gave a rating of 2 or less.

Example 8: Polyethylene / Metallised Polyethylene Terephthalate / Polyethylene Laminate Film

A polyethylene/metallised polyethylene terephthalate/polyethylene laminate film was wrapped around the cork, and then sealed with a heat gun.

Sensory evaluation tests gave a rating of 2 or less.

Example 9: Polyethylene / Polyethylene Vinyl Alcohol / Polyethylene Laminate Film

A polyethylene/polyethylene vinyl alcohol/polyethylene laminate film was wrapped around the cork, and then sealed with a heat gun.

Sensory evaluation tests gave a rating of 2 or less.

Example 10: Polyethylene / Nylon / Polyethylene Laminate Film

A polyethylene/nylon/polyethylene laminate film was wrapped around the cork, and then sealed with a heat gun.

Sensory evaluation tests gave a rating of 2 or less.

Example 11: Polyvinylacetate / Aminosiloxane Emulsion

The cork was dipped into a solution consisting of 75% Polyvinylacetate emulsion and 25% Aminosiloxane emulsion. The coating was then cured in an oven at 38°C for 1 hour.

Sensory evaluation tests gave a rating of 2 or less.

Example 12: Polyvinylidene Chloride / Polymethylhydrogen Siloxane Emulsion

The cork was dipped into a solution consisting of 75% Polyvinylidene chloride and 25% polymethylhydrogen siloxane emulsion. The coating was then cured in an oven at 38°C for 1 hour.

Sensory evaluation tests gave a rating of 2 or less.

WASHING PROCEDURE

Corks can be rinsed or soaked with hot or cold water, alcohol, or a mixture of both water and alcohol, before the coating is applied. This reduces the occurrence of taint and other unwanted odours by washing away any taint compounds already on the surface of the cork. It is thought that any surface taint could mix with the coating during the coating process and remain on the surface of the coating, thus contributing to, rather than preventing, the taint problem. Accordingly, it is preferable to carry out a washing procedure, eg as in Example A, B, C or D below, prior to coating corks. The corks are then dried, eg in an oven at 40°C for 24 hours, prior to being coated.

Example A

Corks spiked with 100mg/L of TCA in absolute ethanol were arranged in a single layer and passed through streams of hot water for 30 seconds and then allowed to dry.

Sensory evaluation tests gave a rating of 2 or less.

Example B

Corks spiked with 100mg/L of TCA in absolute ethanol were arranged in a single layer and passed through streams of liquid containing cold water and absolute ethanol and then allowed to dry.

Sensory evaluation tests gave a rating of 2 or less.

Example C

Corks spiked with 100mg/L of TCA in absolute ethanol were completely immersed in a solution of hot water for 30 minutes and allowed to dry.

Sensory evaluation tests gave a rating of 2 or less.

Example D

Corks spiked with 100mg/L of TCA in absolute ethanol were completely immersed in a solution containing a mixture of cold water and absolute ethanol.

Sensory evaluation tests gave a rating of 2 or less.

METHODS OF APPLICATION**Dip Coating**

The simplest application method is dip coating, involving a container filled with the coating formulation into which the substrate (such as a cork) is immersed and then withdrawn.

A typical dip coating unit consists of a bath, filled with the coating formulation, and a mechanism on which the substrate is mounted for immersion and withdrawal. It is often necessary to circulate and filter the coating to maintain a homogeneous mixture. A fixing mechanism must be designed to ensure the proper orientation of the substrate during immersion into and withdrawal from the fluid.

Spray Coating

In contrast to dip coating, spray coating operations are much less efficient and much more complicated, as well as being relatively more expensive. Precise control over the spray area is difficult so that masking of the substrate may be required. The advantages offered by these systems (eg fast application time, very uniform coating thicknesses, and the ability to apply uniform coatings to irregularly shaped objects) may, however, outweigh the drawbacks.

In a spray coating operation, the fluid is atomised into fine droplets for application to the substrate. The size of the droplets formed during atomisation can be controlled by such properties as fluid flow, fluid pressure, air pressure, solution viscosity, and surface

tension. A number of different nozzle designs are used in industry, such as compressed air spray nozzles, airless spray nozzles, and hot spray systems.

Slot and Curtain Coating

Slot coating and curtain coating are more appropriate techniques for a continuous operation. The methods involve a stationary die, which delivers a layer of coating onto a substrate moving beneath it. The difference between the methods is in the way that the coating is transferred from the die to the moving substrate. The coating is spread by the slot method when the die slot is close to the substrate; but changing the orientation of the die slot relative to the conveyor and allowing the formulation to cascade is referred to as curtain coating.

Multiple slots in the die face or converging feed to a single slot can produce multilayer coatings.

Roll Coating

Roll coating is another method used in continuous manufacturing operations primarily for coating films. A substrate is fed between two rotating cylinders, while simultaneously directing the coating into the space between the cylinders. Formulation viscosity, speed of the substrate, coating flow rate, and distance between the rolls all contribute to coating thickness and uniformity. Although these systems are limited in the types of substrate that can be coated, they can rapidly produce a very uniform product.

METHODS OF CURING

Thermal Cure

One of the most common methods for initiating the cross-linking of a polymer is by heating, and ovens can be incorporated into batch and continuous-mode systems. The main disadvantage in thermal curing is the wasted thermal energy when only a small amount of the applied energy is transferred to the molecules. It can also be difficult to maintain a uniform temperature throughout the oven, so that curing may be uneven.

Ultraviolet (UV) Cure

One of the most popular techniques used to initiate cross-linking is irradiation by ultraviolet light. It can be a more rapid process than thermal curing, sometimes taking less than a second to act. Very little heat is generated during the exposure, which can often be carried out at room temperature.

Electron Beam Cure

Electron beam (E-beam) radiation shares the same benefits as UV radiation, without the need for a photoinitiation. The exposure forms free radicals that cause the chain reaction.

Gamma-Radiation Cure

Yet another type of irradiation that is rapid at ambient temperatures is γ -radiation cure. Cycle times for γ -ray systems can be longer than for E-beam, at least for conventional polymer matrices, but for curing hydrophilic coatings this does not present a problem.

ADDITIONAL TECHNOLOGIES**Plasma Polymerisation**

Thin polymer films can be deposited onto various substrates through the use of plasma polymerisation. A plasma is generated by means of electron excitation, with a gas mixture and an organic monomer. These thin films can be between a few hundred angstroms to a micrometre in thickness. Cross-linking density is usually greater than in conventionally applied coatings, and thin films exhibiting good adhesion can be laid down on virtually any type of substrate.

Surface Grafting

Surface grafting techniques incorporate some of the same general concepts as coating and curing operations but may be more appropriate where exceptionally thin surface layers are desired. Points that distinguish surface grafting from "wet" coating operations are related mainly to the formation of the modified surface layer and the

general molecular structures that result. In conventional coatings, a continuous phase is formed by the reactions of the monomeric or polymeric ingredients, and is adhered to the substrate surface through secondary molecular interactions such as hydrogen bonding, London dispersive forces or acid-base interactions. Primary covalent bonding is also possible if the substrate has been pre-treated with molecular groups. In surface grafting however, the monomeric (or polymeric with reactive end groups) components react directly with a polymeric substrate. Various forms of radiation, such as UV, electron beam, and γ -rays, may be used to cause the formation of peroxide groups on the polymer surface. These are unstable so decompose, and cause initiation of polymerisation in the process.

While the present invention has been described in terms of preferred embodiments in order to facilitate better understanding of the invention, it should be appreciated that various modifications can be made without departing from the principles of the invention. Therefore, the invention should be understood to include all such modifications within its scope.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for producing a coating or diffusion layer on a substrate for use in contact with a food product or beverage, said coating or diffusion layer preventing or inhibiting passage therethrough of flavour-active or odour-active compounds, and said method comprising applying to the surface of said substrate an effective amount of a barrier polymer, said barrier polymer being a polymeric material, the molecular structure and/or morphology of which prevents or inhibits passage therethrough of flavour-active or odour-active compounds.
2. A method according to claim 1, wherein said substrate is a bottle closure, packaging or wrapping material, or a bottle or other container.
3. A method according to claim 1, wherein said substrate is a natural or synthetic cork, and said coating or diffusion layer prevents or inhibits passage of flavour-active or odour-active compounds from said cork to an alcoholic beverage in contact with said cork.
4. A method according to claim 1, wherein said flavour-active or odour-active compounds are trichloroanisoles (TCA).
5. A method according to claim 1, wherein said barrier polymer is a polymer with low oxygen permeability.
6. A method according to claim 1, wherein said barrier polymer is a polyurethane or a copolymer or ionomer thereof, polyethylene terephthalate (PET), polyethylene vinyl alcohol, polyvinyl alcohol, polyacrylonitrile or a copolymer thereof, polyvinylidene chloride or a copolymer thereof, polyvinyl chloride or a copolymer thereof, Cellophane, Saran, an epoxy polymer, a siloxane copolymer, a mono-, di- or poly- functional silane or a copolymer thereof, a polyamide or a copolymer thereof,

polychlorotrifluoroethylene, bisphenol A (BPA) - epichlorohydrin, polyacetal, polyvinyl fluoride, polymethylmethacrylate or a copolymer thereof, cellulose nitrate or a derivative thereof, poly(isobutylene) or a copolymer thereof, polyisoprene, polyvinylacetate (PVA) or a copolymer thereof, polybutadiene or a copolymer thereof, a laminate film comprising polyethylene, polyethylene terephthalate (PET), polyethylene vinyl alcohol and/or polyamide copolymers, or a functionalised or unfunctionalised polysilsesquioxane.

7. A method according to claim 6, wherein said barrier polymer is polyethylene vinyl alcohol, a polyurethane or a copolymer or a ionomer thereof, a siloxane copolymer, a mono-, di- or poly-functional silane or a copolymer thereof, polybutadiene or copolymer thereof, or a laminate film comprising polyethylene, polyethylene terephthalate (PET), polyethylene vinyl alcohol and/or polyamide copolymers.
8. A coated substrate produced according to the method of any one of claims 1 to 7.
9. A coated cork produced according to the method of any one of claims 1 to 7.
10. A method according to any one of claims 1 to 7, substantially as described herein and with reference to any one of Examples 1 to 12.
11. A coated substrate according to claim 8, substantially as described herein and with reference to any one of Examples 1 to 12.
12. A coated cork according to claim 9, substantially as described herein and with reference to any one of Examples 1 to 12.

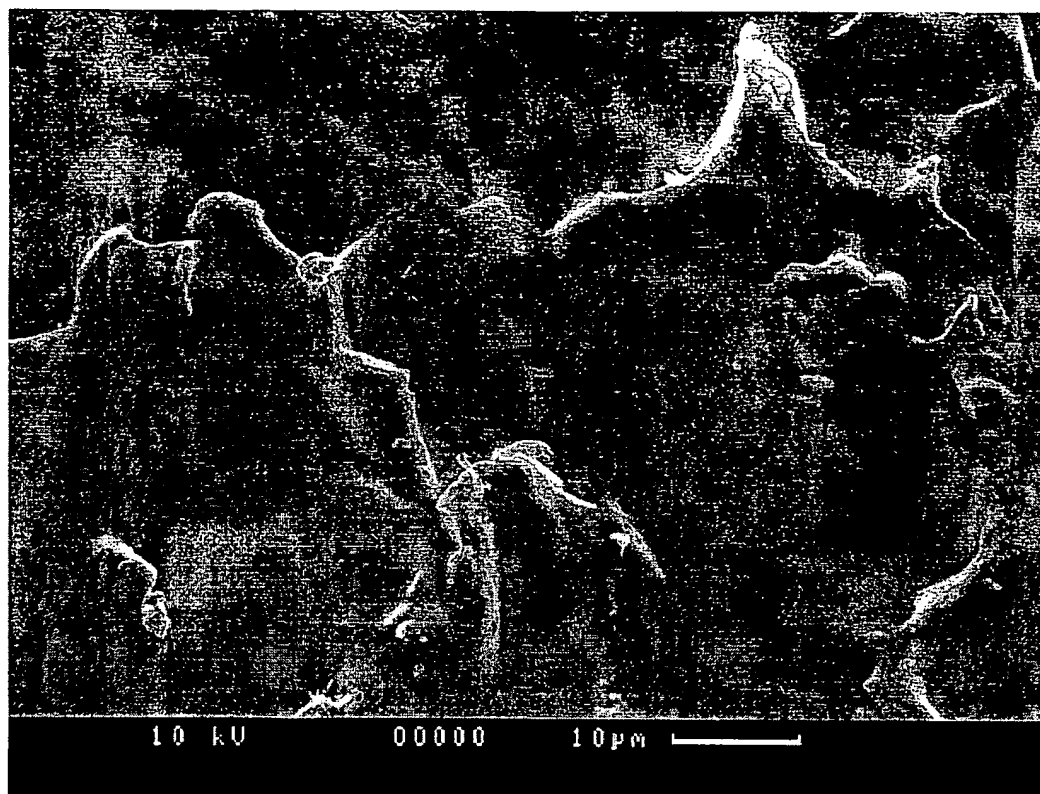


FIG 1

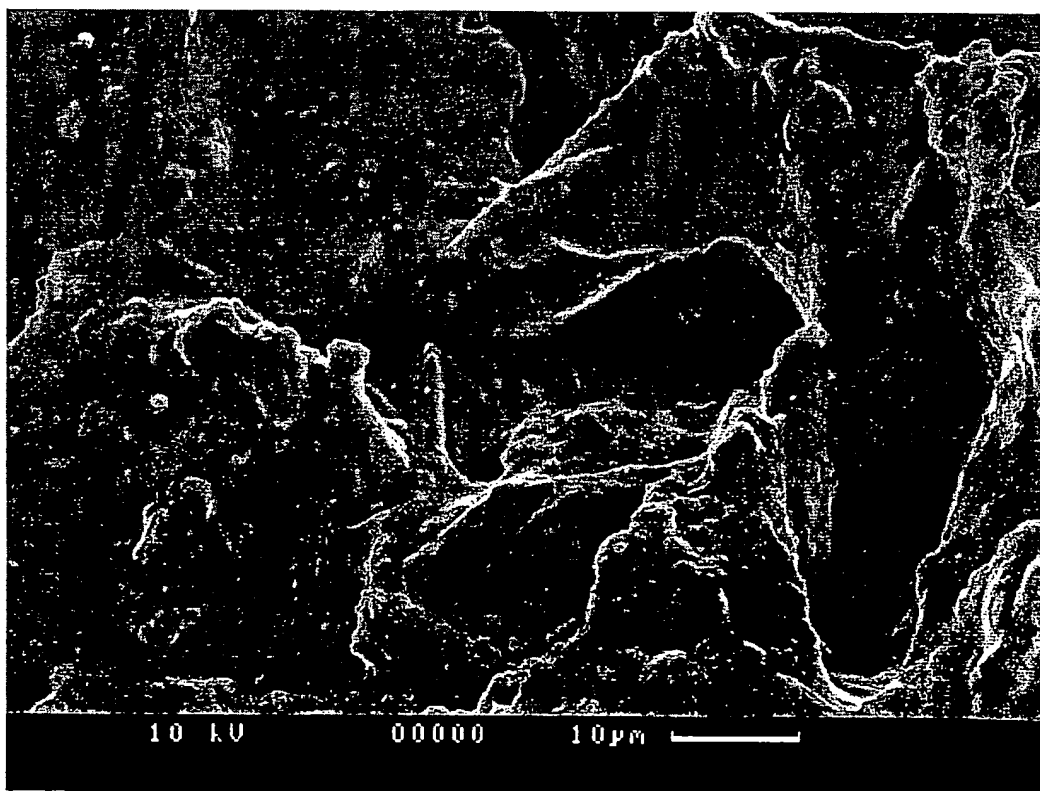


FIG 2

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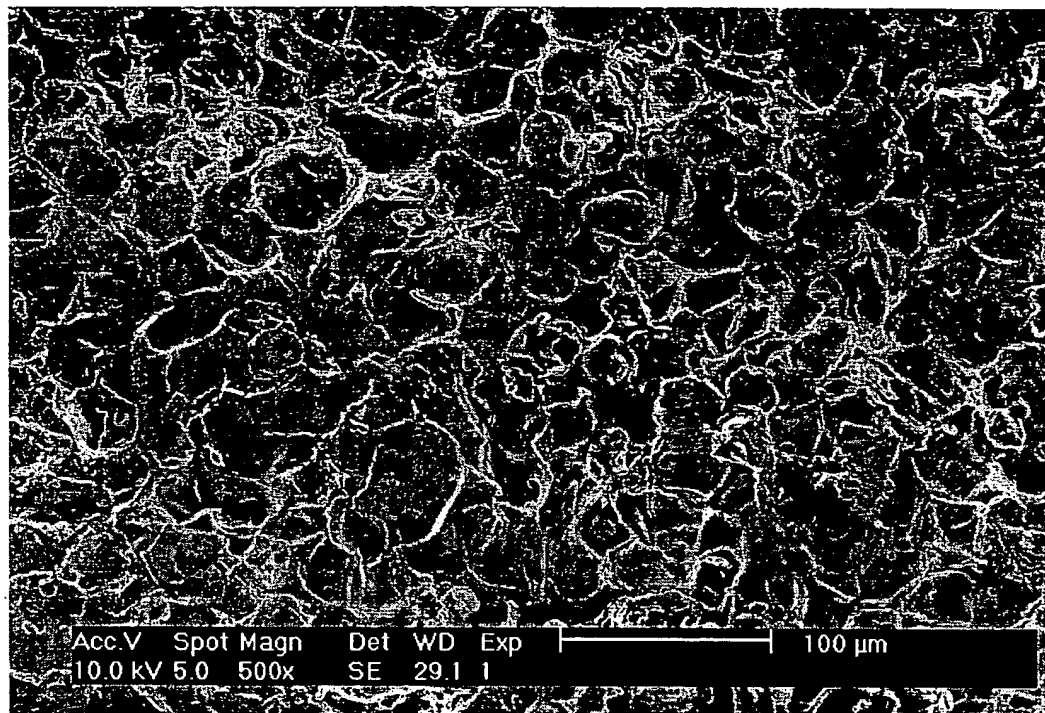


FIG 3A

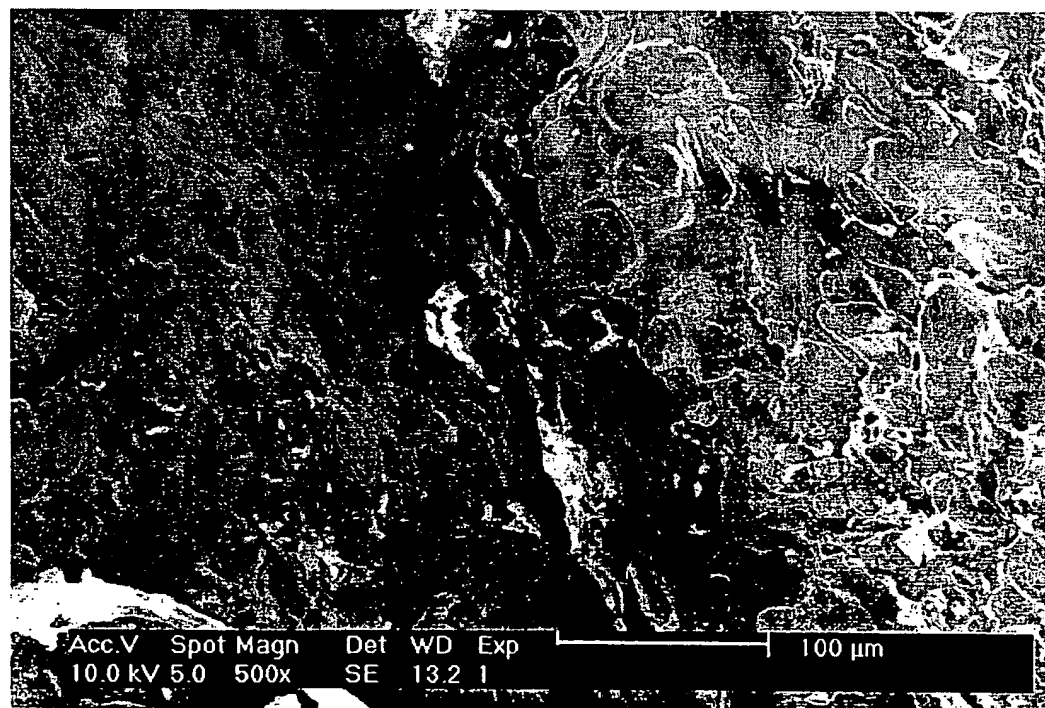


FIG 3B

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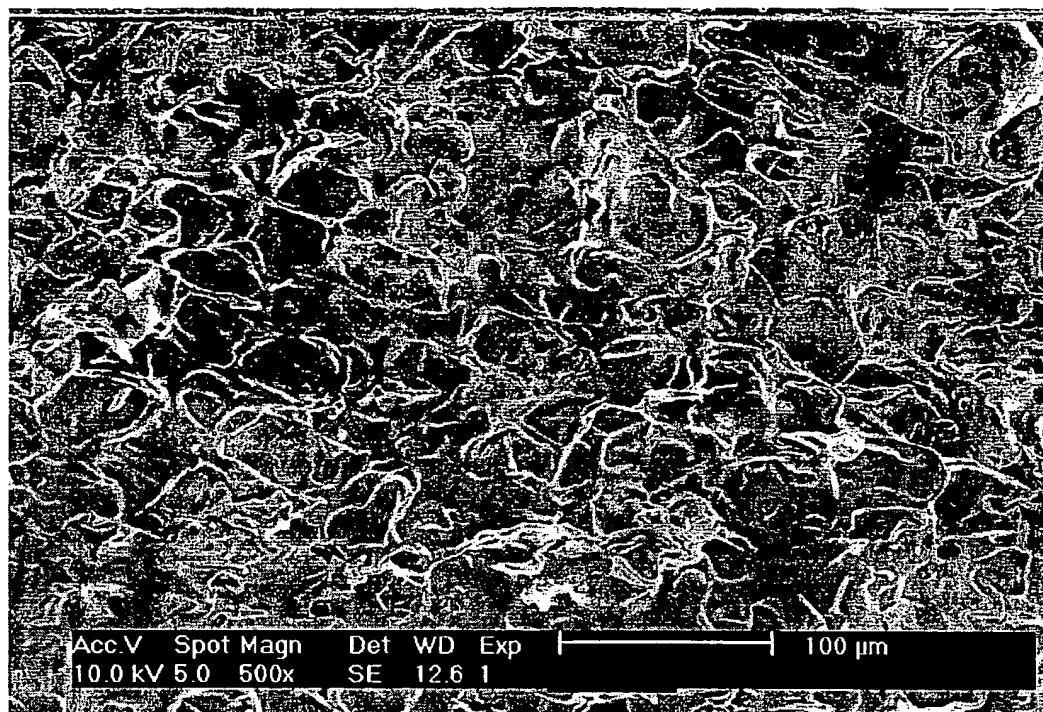


FIG 3C

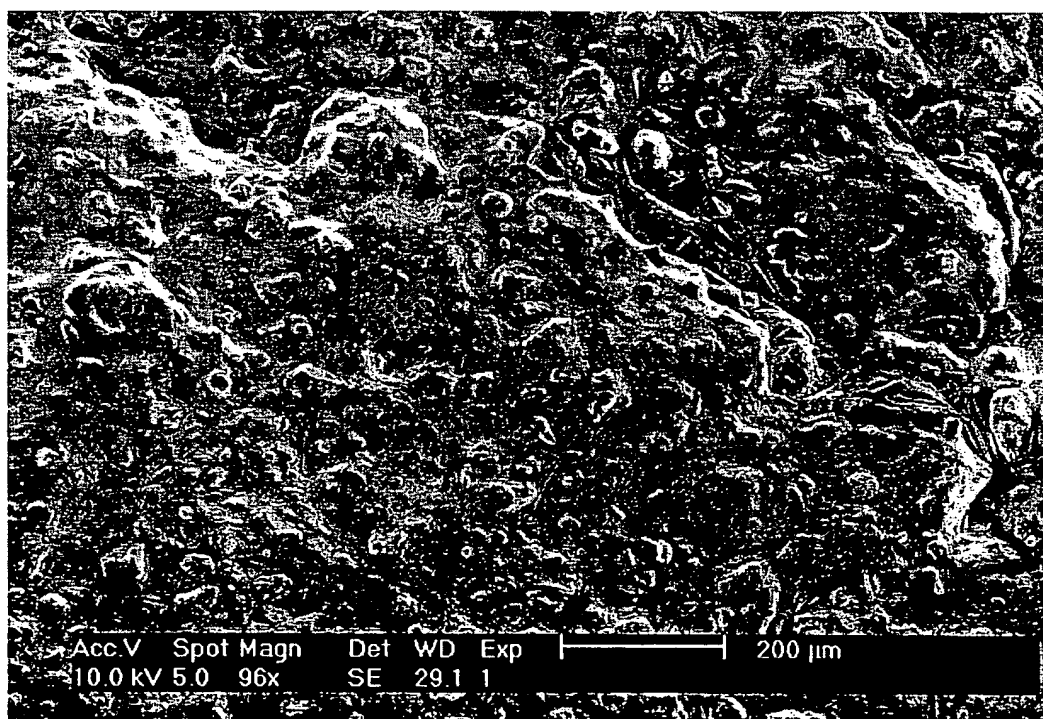


FIG 3D

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00365**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl. ⁷: B27K 7/00, B67B 1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC B27K 7/00, B67B 1/03, 1/02, B65D 23/02, 25/14, 39/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC AS ABOVEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT WPAT**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/28378 A (DEWCO INVESTMENTS PTY. LTD.) 19 September 1996 see whole document	1-12
X	WO 97/11894 A (FULLER JP) 3 April 1997 see abstract	1-12
X	AU 47995/85 A (JONES, STEAINS AND WALLER (N.S.W.) PTY. LTD) 10 April 1986 see claims	1-12

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
8 June 2000Date of mailing of the international search report
26 JUN 2000Name and mailing address of the ISA/AU
AUSTRALIAN PATENT OFFICE
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MATTHEW FRANCIS
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00365

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	Derwent Abstract Accession No. 99-529425/45, Class A92 (A14 A17 A26), DE 29912842 A (GUELTIG KORKWARENFABRIKATION GMBH) 22 July 1999	1-12
X	WO 97/30122 A (CELLRESIN TECHNOLOGIES, L.L.C.) 21 August 1997 see abstract, claims	1, 2, 5-8
X	US 4254170 A (ROULLET) 3 March 1981 see abstract, claims	1, 2, 5-8
X	EP 39626 A1 (TOYO SEILAN KAISHA LIMITED) 11 November 1981 see abstract, claims	1, 2, 5-8
X	WO 97/01427 (VALYI EI) 16 January 1997 see abstract, claims	1, 2, 5-8
X	US 5576068 A (CABURET) 19 November 1996 see whole document	1, 2, 5-8
X	EP 423511 A1 (TETRA PAK HOLDINGS & FINANCE S.A.) 24 April 1991 see whole document	1, 2, 5-8
X	EP 341937 A2 (INTERNATIONAL PAPER COMPANY) 15 November 1989 see whole document	1, 2, 5-8
X	EP 538774 A2 (TOYO BOSEKI KABUSHIKI KAISHA) 28 April 1991 see abstract, claims	1, 2, 5-8

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00365

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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US	5576068	EP	823933	FR	2733758	WO	9634926
EP	423511	AU	64649/90	CA	2027352	JP	3153348
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		US	4940612	US	4888222	US	4880701
		US	4921733				
EP	538774	JP	5112755	US	5288559		
END OF ANNEX							